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FOR THE DETERMINATION OF INTERATOMIC POTENTIALS

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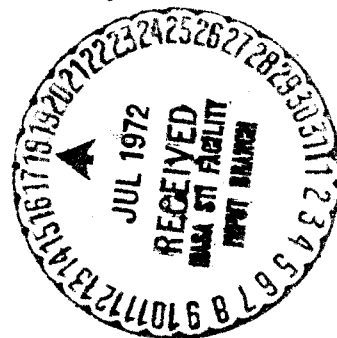
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<u>Page</u>	<u>Location</u>	<u>Change to read</u>
5	line 3	After 9.4 Å), add sentence: (However, there is a stated ^{20b} uncertainty of some 25% in the Buck-Pauly potential at 9 Å.)
22	Bottom	Add paragraph: Finally, the precision attainable in the determined parameters (such as $\epsilon^2_{r_m}$ and ϵ) is limited by the degree of precision of $A_1, \dots,$ A_4, H_1 from Table II. For example, using Model I and Eq. (17b), the statistical uncertainty in the determined value of ϵ will be at least $\pm 8\%$ under the best of conditions.
24	line 5	Degree Fitted ^f
25	Bottom line	case E , $\beta = 1 \text{ Å}^{\text{O}2}$.
27	line 2	what similar in shape, ...
34	Ref. 19(a)	J. Chem. Phys. <u>56</u> (1972), in press.
35	Ref. 36	(a) U. Buck (etc.) (b) U. Buck, private communi- cation (1972); to be published.

OPTIMAL UTILIZATION OF TOTAL ELASTIC SCATTERING CROSS SECTION DATA
FOR THE DETERMINATION OF INTERATOMIC POTENTIALS*

R. B. Bernstein and R. A. LaBudde

Theoretical Chemistry Institute and Chemistry Department
University of Wisconsin, Madison, Wisconsin 53706

ABSTRACT

With the advent of improved experimental data on absolute total cross sections $Q(v)$ for atom-atom collisions and their velocity dependence, on the glory undulations and the transition to high-velocity behavior, it is timely to reconsider the problem of inversion of such data to yield information on the interatomic potential. In the absence of additional data in the form of differential cross sections there is a limit to the amount of information available from $Q(v)$ even when observations of good accuracy (e.g., $\pm 0.25\%$) are in hand over an extended energy range (e.g., from "thermal" energies upward by a factor of $\gtrsim 10^3$ in relative kinetic energy). A number of commonly used procedures for data inversion are no longer adequate to deal optimally with the high quality experimental results now becoming available. The present paper attempts to develop improved methods for data utilization, which take full advantage of the accuracy of the experimental $Q(v)$ measurements.

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I. INTRODUCTION

It was recognized in 1934 by Massey and Mohr¹ that total cross sections for the elastic scattering of atoms by atoms could yield information on the interatomic forces, particularly the long-range part of the interaction potential. At about the same time the experimental (beam) techniques for making such measurements (as originated by Born,^{2a} Bietz^{2b} and Knauer and Stern^{2c} in Germany during the previous decade) were brought to fruition quantitatively by Mais, Rosin and Rabi³ in the U.S.A., by Sasaki, Nishibori, Koderu and co-workers⁴ in Japan and by Fraser and Broadway⁵ in England. In 1935 the status of the subject as a "new kinetic theory of gases" was established in a summary by Rabi,^{6a} which complemented an overall review on molecular beam scattering by Guillemin.^{6b} In 1936 Massey and Buckingham⁷ showed how existing total cross section data for alkali-rare gas systems could be utilized to ascertain the magnitude of the long-range, London dispersion " C_6 constant," i.e., the coefficient of the asymptotic attractive potential $V(r) \sim -C_s/r^s$, where for S-state atoms $s = 6$. These experimentally-derived coefficients compared well with theoretical estimates based on the Slater-Kirkwood-Hellmann (SKH) approximations.

A rather small number of experimental studies on total cross sections were carried out over the next two decades, however. One of the more extensive of these was a series of measurements (and theoretical correlations) of total cross sections for the scattering of numerous atom-atom and atom-molecule systems, reported in 1959.⁸ All of the experiments up to this time had involved the scattering of thermal (Maxwellian) beams by thermal "target" gases, so that the resulting cross sections were all heavily velocity-averaged. However, the interesting possibility of verification of the asymptotic interatomic force law, i.e., determination

of the inverse power s in the long-range potential, from the velocity-dependence of the cross section had been known since the appearance of the original Massey-Mohr (MM) equation,¹ which can be written in the form

$$Q(v) = p_{mm}(s) (C_s/hv)^{\frac{2}{s-1}} \quad (1)$$

Here the constant of proportionality $p_{mm}(s)$ is a known, slowly-varying function of s , and v is the relative velocity.

In 1960 the first experimental study of the velocity-dependence of the total cross section was reported, by Pauly,⁹ for the K-N₂ system. Here s was found to be 6 (within an uncertainty of about 10%), confirming the theoretical expectation, thus indirectly establishing confidence in the procedure for determining C_6 values from "absolute" values of thermally-averaged total elastic scattering cross sections.

Three sources of doubt remained, however, in the resulting potential constants C_6 . One involved the possibility of systematic experimental errors in the cross sections. This suggested itself from the fact that many of the experimentally-derived C_6 constants were significantly larger than theoretically estimated (SKH) values, although ratios of C_6 values were in excellent agreement with theory.¹⁰ The source of this error¹¹ was determined and previous experimental results corrected as required.^{11a} The revised C_6 constants accorded well with SKH-approximated values, and even better with the more rigorous perturbation-theory results of Dalgarno and co-workers.¹²

Another source of doubt was the validity of the MM approximation in general, and in particular the magnitude of the constant $p_{mm}(s)$ in Eq. (1). Even on the assumption of a pure r^{-6} potential, several different approxi-

mation formulas had been derived in the literature,¹³ each having employed somewhat different assumptions. All of these yielded the same functional form of the velocity dependence as the MM equation, but slightly different coefficients $p(s)$. Table 1 lists the values of $p(6)$ thus obtained. Not included are results of three other approximate treatments,¹⁴ based on the application of the uncertainty principle, which lead to the same MM form but whose p values are inherently less accurate.

Table 1. Values of $p(6)$ according to different approximations

	<u>Massey-Mohr</u> ¹	<u>Firsov</u> ^{13a}	<u>Schiff</u> ^{13b}	<u>Landau-Lifshitz</u> ^{13c}
$p(6):$	7.547	8.037	8.083	8.083

On the basis of a comparison with sample exact calculations (for a pure repulsive r^{-12} -power potential) it was concluded^{13d} that the Schiff-Landau-Lifshitz (SLL) coefficient p_{SLL} was to be preferred over p_{MM} . However, the entire range of $p(6)$ values of Table 1 is only 7.1%, so that in any case the uncertainty in the derived C_6 from a given Q is confined to a span of ca. 18%.

A third source of doubt was the possible influence of the next higher-order terms in the long-range potential, e.g., the r^{-7} retardation term and/or the r^{-8} dipole-quadrupole contribution. A perturbation-like treatment of these effects on the total cross section has been carried out,¹⁵ which indicated that the more important effect (at "thermal" conditions) was due the r^{-8} term, the incremental cross section being approximately $\frac{2}{3}\pi\beta$, where $\beta = C_8/C_6$. Recent theoretical calculations of β by Davison,¹⁶ though significantly larger than values from the older literature, have led to the conclusion¹⁶ that the r^{-8} term makes only a small

contribution to the cross section at thermal energies for the typical systems investigated. Nevertheless, the presence of this extra contribution to the cross section, which is to a first approximation velocity-independent,^{15a} could make itself known via a deviation from the $v^{-2/5}$ form of $Q(v)$ (cf. Eq.(1)). This type of deviation was observed by Beck and Loesch¹⁷ for the K-Kr and K-Xe systems. The direction and magnitude of the effect was in accord with that expected on the basis of Refs. 15a and 16. However the results cannot be considered to be definitive evidence for the C_8 contribution, since any additive attractive contribution to the potential over and above the asymptotic form $V \sim -C_6/r^6$ would introduce a qualitatively similar deviation from the $v^{-2/5}$ velocity dependence. It is therefore difficult to extract from $Q(v)$ data definitive information on such "correction terms" to the r^{-6} potential tail.

Schlier and co-workers¹⁸ have shown by means of calculations based on a flexible model potential (termed "realistic") that the \bar{Q} , averaged over the glory undulations, can differ significantly from the Q_{SLL} based upon the C_6 assumed for the model potential. This is presumably due to the fact that the range of r probed by the Q measurements (over the velocity range considered) extended inward to smaller separations than those for which the potential could be well approximated by its asymptotic form, i.e., in the region of r near $(Q/2\pi)^{1/2}$, $V(r) \neq -C_6/r^6$.

A clear experimental indication of this difficulty is seen from the recent work of Pauly and associates.¹⁹ For the systems Na⁻, K⁻, and Cs-Hg for which a full "Buck-inversion"²⁰ of all scattering data has yielded the "true" potentials,^{19a,20b} Buck et al.^{19a} showed that even at their largest reduced separation $z = r/r_m = 2$, where $|V|/\epsilon \cong 0.015$, the $C_8 r^{-8}$ and higher terms constitute a significant contribution to the

potential. Specifically, for Na-Hg, using the best theoretical estimate for C_6 ²¹ one calculates that the $C_6 r^{-6}$ term accounts for only slightly more than half the total potential^{20b} at this separation (of 9.4Å).

This result, if found to be representative,²² would call into question the practical usefulness of the long-range perturbation expansion in reciprocal powers of r . Certain and Bruch,²³ reviewing the question of the validity of the long-range expansion, indicate that the higher multipole terms (i.e., C_8 , C_{10} etc.) become important at about the same r as the exponential overlap terms. They state that "it rarely makes sense to include higher order multipole terms while neglecting overlap terms". One might say that when the leading term does not suffice, the usefulness of the series expansion is doubtful. Nevertheless one must be careful not to "throw out the baby with the bath water". At present, total cross sections constitute the only "direct" source of information about the C constants and have, on the whole, yielded values in fair accord with theory. Croucher and Clark²⁴ compare all available theoretical and experimental (i.e., from thermal Q data) C_6 values for alkali atom interactions with atoms and non-reactive diatomics; with a few notable exceptions²⁵ the results are within mutual uncertainty limits. Clearly the dominant term in the total cross section is that due to the asymptotic C_6 coefficient. However, a proper inversion of $Q(v)$ data is highly desirable. Attempts in this direction by several workers²⁶ have not yet been put into practice.

Irrespective of this problem (the higher-order deviations from a pure r^{-6} -dependence in the range of r probed by thermal $Q(v)$ measurements), the influence of the potential well and the short-range repulsive force is a separate and important question. It was pointed out in 1961^{27a} that extrema in the velocity dependence of the cross section for atom-atom

scattering would thereby be expected. These "glory undulations" could be understood^{27c,28} from semiclassical considerations,²⁹ and the extrema indexed unambiguously.²⁷ A Jeffreys-Born (JB) (high-energy) approximation for the velocity-dependent maximum phase shift η_m was derived^{27b,c}, making it possible to express the index N of the glory extremum as a linear function of $\frac{1}{v_N}$ (valid in the high-velocity limit). Here v_N is the velocity of the N th glory extremum, determined from a plot of $\Delta Q = Q - \bar{Q}$ vs. $1/v$ (where \bar{Q} is the local mean of Q , averaged over the undulations) or of $vQ^{5/2}$ [or $(C_6)_{app}$] vs. $1/v$ (where $(C_6)_{app}$ is the apparent C_6 value assuming a dominance of the r^{-6} term in $V(r)$ and Eq. 1 and a $p(6)$ from Table 1). The limiting form of $\eta_m(v)$ ²⁷ suggested that the slope of a plot of $N - \frac{3}{8}$ vs. v_N^{-1} (say I) is proportional to the product ϵr_m :

$$I = \left(\frac{2a_1}{\pi\hbar} \right) \epsilon r_m, \quad (2)$$

where a_1 is a constant which depends upon the functional form of $V(r)$.

The quantity a_1 was evaluated for several realistic model potentials:³⁰

it varied over the range 0.34 - 0.50 for the cases examined, and was

found to depend primarily on the reduced curvature, κ , of the potential minimum (being less sensitive to other features of potential functions).

Thus, on the assumption of a functional form or model potential, for which

a_1 was known, ϵr_m could be evaluated from the measured I or

$$a_1 \epsilon r_m.$$

In an attempt to extract further information from the glory-velocities, Bernstein and O'Brien carried out a higher-order expansion of η_m in terms of reciprocal powers of velocity and of energy,³⁰ assuming various model potentials. Out of this arose an improved procedure for utilizing precise extrema data which involved a graph (designated³¹ a BOB plot) of $(N-\frac{3}{8})v_N$ vs. $1/E_N$ (where $E_N = \frac{1}{2}\mu v_N^2$), whose intercept is the I of Eq.(2) and "limiting slope" S_1 . For the commonly used model potentials it was found that the quantity $\epsilon^2 r_m$ could be directly determined from S_1 , essentially independent of κ (to be contrasted with the relation between ϵr_m and I , via the a_1 of Eq.(2)).

The BOB procedures were criticized by several workers, however, on several counts. First, as recognized from the outset, it did not take advantage of data on the glory amplitudes, which contain information on the potential.²⁸ Second, the deduction³⁰ that a_1 depended primarily upon the curvature κ was empirical, based only on a few simple model potentials. The failure of this correlation was pointed out by Dürren and Schlier^{18a} by the counterexample of a flexible, multiparameter, potential for which κ could be varied independently of a_1 . The most penetrating analysis was that of Mason, Munn et al.³² who showed the origin of glory undulations by an optical analogy. They found that the extrema-spacing (and thus a_1) is better-correlated with the (reduced) "area" of the potential well than with κ , so that to a fair approximation (i.e., within a range of $\pm 20\%$ for all model potentials tested, including the pathological square-well):

$$I \propto \int_{\sigma}^{\infty} V(r) dr, \quad (3)$$

where σ is the (usual) zero of the potential. Third, in the case of the alkali-Hg systems, certain discrepancies have arisen. For Li-Hg the potential derived from $Q(v)$ data and a BOB-treatment by Rothe and Veneklasen³³ (as extended by Olson,^{34a} whose analysis took cognizance of some angular distribution data^{34b}) appears to violate the empirical "Similar Potential Hypothesis" of Stwalley,³⁵ when compared with the Na-Hg and K-Hg potentials. A still more damaging finding was that of Buck et al.^{19b} who compared the potential parameters of Na-Hg estimated from a BOB analysis of their $Q(v)$ data with the "true values" (from a full "Buck-inversion"), and found a discrepancy of some 20% in $\epsilon^2 r_m$. They attributed this³⁶ to a difference in the BOB expansion coefficients (for η_m) characterizing the actual $V(r)$ for the alkali-Hg systems, and those for the model potentials of Ref. 30. At this stage it therefore becomes necessary to face the main question directly: given extensive data, of good (but finite) accuracy, on glory extrema in the thermal energy (so-called "low-velocity") range, i.e., $Q(v)$ as discussed, how much information on the interatomic potential is available, i.e., how much can be extracted from such data, and what is an optimal procedure to accomplish this goal? The present paper addresses itself to this problem.

II. FORMAL RELATIONSHIPS

The total cross section $Q(v)$ is assumed to be a sum of two components: a smoothly varying $Q(v)$, dependent primarily upon the long range potential constant C_6 , and $\Delta Q_g(v)$, an oscillatory term, causing the glory extrema:^{27,28}

$$Q(v) = \bar{Q}(v) + \Delta Q_g(v) \quad (4a)$$

where $\bar{Q}(v) \cong Q_{sLL}(v)$ of Eq.(1) and

$$\Delta Q_g(v) \cong \frac{4\pi^{3/2}}{k^2} \frac{L_g}{(-\eta_m'')^{1/2}} \sin\left(2\eta_m - \frac{3\pi}{4}\right), \quad (4b)$$

where, as usual v is the relative velocity, $k = \mu v/\hbar$ is the associated wavenumber, L_g is the glory angular momentum, i.e., the value of the orbital quantum number ℓ corresponding to η_m , the maximum phase shift, and η_m'' is the second-derivative of η_m with respect to ℓ evaluated at $\ell = L_g$.

Introducing the reduced variables^{27c,d}

$$\eta_m^* \equiv \eta_m / k r_m$$

$$\beta_g \equiv L_g / k r_m,$$

where r_m is, as usual, the position of the minimum of $V(r)$, Eq.(4b) may be rewritten:

$$\Delta Q_g(v) = (\pi r_m)^{3/2} 4k^{-1/2} \frac{\beta_g}{\left[-\frac{d^2 \eta_m^*}{d\beta_g^2} \right]^{1/2}} \sin\left(2k r_m \eta_m^* - \frac{3\pi}{4}\right) \quad (5)$$

Consider the following expansions^{30,37,38} based upon the high-velocity limit:

$$\eta_m^* = \frac{a_1}{E^*} + \frac{A_1}{E^{*2}} + \frac{A_2}{E^{*3}} + \dots \quad (6a)$$

$$\beta_g = B_0 + \frac{B_1}{E^*} + \frac{B_2}{E^{*2}} + \dots \quad (6b)$$

$$-\left. \frac{d^2 \eta_m^*}{d\beta^2} \right|_{\beta_g} = \frac{c_1}{E^*} + \frac{C_1}{E^{*2}} + \frac{C_2}{E^{*3}} + \dots, \quad (6c)$$

where $E^* (\equiv K) = E/\epsilon$ is the usual reduced energy (ϵ being the depth of the potential well).

It was shown^{30a} that a_1 , B_0 , and c_1 are constants determined by the reduced curvature of the potential and that $A_1, A_2, \dots, B_1, B_2, \dots, C_1, C_2, \dots$, can be taken as constants independent of the form of the potential and of K , ϵ and r_m , at least within a certain class of parameterized potentials. Under the (strong) assumption that they are essentially "universal constants", the unknown character of η_m^* , β_g , and $\left[\frac{d^2 \eta_m^*}{d\beta^2} \right]_{\beta_g}$ is completely specified by the values of a_1 , B_0 , and C_1 . The following expansion is more pertinent for the purpose of obtaining ΔQ via Eq. (5) than the expansion of β_g and $\left[\frac{d^2 \eta_m^*}{d\beta^2} \right]_{\beta_g}$ of Eqs. (6b,c):

$$\beta_g \left[-\left. \frac{d^2 \eta_m^*}{d\beta^2} \right|_{\beta_g} \right]^{-1/2} = g_0 E^{*1/2} \left[1 + \frac{H_1}{E^*} + \frac{H_2}{E^{*2}} + \dots \right], \quad (7)$$

where $g_0 = B_0/c_1^{1/2}$. As for the A's, B's, etc., it will be seen below that H_1, H_2, \dots , are essentially independent of the form of the potential, within the same class of parameterized potentials. Combining Eqs. (5), (6a) and (7) leads to a simple expression for the glory contribution:

$$\Delta Q_g(v) = (2\pi r_m)^{3/2} g_0 \left(\frac{\hbar v}{\epsilon} \right)^{1/2} \left[1 + \frac{H_1}{E^*} + \frac{H_2}{E^{*2}} + \dots \right] \sin \phi, \quad (8a)$$

where

$$\phi = 2kr_m \eta_m^* - \frac{3\pi}{4} = \frac{4\epsilon r_m}{\hbar v} \left(a_1 + \frac{A_1}{E^*} + \frac{A_2}{E^{*2}} + \dots \right) - \frac{3\pi}{4}. \quad (8b)$$

The problem of evaluating $\bar{Q}(v)$ of Eq. (4a) remains. Formally we may write

$$\bar{Q}(v) \equiv Q_{SLL}(v) + \delta Q(v), \quad (9)$$

where $\delta Q(v)$ is the "correction" for the higher order terms in the inverse power expansion for $V(r)$, which may be expected to be slowly-varying.

Fully aware of the caveats mentioned in Séc. I, one can attempt to approximate this correction assuming only the dipole-quadrupole contribution.

It has been shown previously^{15a} that when the $C_8 r^{-8}$ term in the potential begins to affect the cross section, its effect is to introduce an additive correction to Q , essentially velocity-independent, namely

$$\delta Q(v) \equiv \delta^{(8)} Q \approx \frac{2\pi}{3} C_8 / C_6. \quad (10)$$

Values of the C_8/C_6 ratio¹⁶ range typically from 2.7\AA^2 for the He-He³⁹ to 28\AA^2 for Cs-Cs, so the C_8 contribution to \bar{Q} should be fractionally small, though not negligible (see, however, Ref. 25). As discussed in

III. DETERMINATION OF THE EXPANSION COEFFICIENTS

Using the tabulated values of η_m^* , β_g , and $[d^2 \eta_m^* / d\beta^2]_{\beta_g}$ given by O'Brien³⁷ the values of the coefficients (A_i, B_i, C_i, H_i) were determined in the following way: the reference potential was taken to be of the standard L.-J. (12,6) form, although for the purpose of comparison the calculations were repeated for an Exp(α ,6) potential, with $\alpha = 13.772$.

Using 20 tabulated points in the range $1 \leq E^* \leq 100$, for each of Eqs. (6a), (6b), (6c) and (7) a weighted (assumed constant relative error) forward curvilinear regression was carried out for the pertinent quantities (i.e., η_m^* , β_g , etc.) with a_1, B_0 , and c_1 held fixed at their theoretical known values. The regression was stopped when the next term to be added was not significant at the 90% level (via the F-test). The results are given in Table II. It was found that reproduction to full accuracy of η_m^* was obtained by including terms to A_4 in (6a), and of $\beta_g / [-d^2 \eta_m^* / d\beta^2]_{\beta_g}^{1/2}$ using only the term H_1 in (7).

In terms of these truncated forms, Eq. (8) becomes

$$\Delta Q_g(v) \cong (2\pi r_m)^{3/2} g_0 \left(\frac{\hbar v}{E} \right)^{1/2} \left(1 + \frac{H_1 E}{E} \right) \sin \phi, \quad (11a)$$

where

$$\phi \cong -\frac{3\pi}{4} + \frac{4\epsilon r_m}{\hbar v} \left(a_1 + \frac{A_1 \epsilon}{E} + \frac{A_2 \epsilon^2}{E^2} + \frac{A_3 \epsilon^3}{E^3} + \frac{A_4 \epsilon^4}{E^4} \right). \quad (11b)$$

Isolating the velocity dependence and assuming H_1, A_1, \dots, A_4 to be constants, Eq. (4) becomes (in the limit $\sqrt{Q(v)} \rightarrow 0$):

$$Q(v) \cong \gamma_1 v^{-2/5} + \gamma_2 v^{1/2} \left(1 + \frac{\epsilon H_1}{E} \right) \sin \phi \quad (12a)$$

with

$$\phi = -\frac{3\pi}{4} + \frac{\gamma_3}{v} + \frac{\gamma_4}{vE} \left(A_1 + \frac{E A_2}{E} + \frac{E^2 A_3}{E^2} + \frac{E^4 A_4}{E^3} \right), \quad (12b)$$

where

$$\gamma_1 = p_{\text{SLL}}(6) (C_6/\hbar)^{2/5} \quad (13a)$$

$$\gamma_2 = (2\pi r_m)^{3/2} g_0 (\hbar/\epsilon)^{1/2} \quad (13b)$$

$$\gamma_3 = 4 a_1 \epsilon r_m / \hbar \quad (13c)$$

$$\gamma_4 = 4 \epsilon^2 r_m / \hbar \quad (13d)$$

and ϵ are free parameters.

Thus, given C_6 , g_0 , a_1 , r_m , and ϵ , then $\gamma_1, \dots, \gamma_4$ may be calculated from Eqs. (13), using $p_{\text{SLL}}(6) = 8.083$ from Table 1, and the total cross section as a function of velocity given by Eqs. (12). Table III shows a comparison of $Q(v)$ calculated from Eq. (12) for a specified L.-J. (12,6) potential with computed JWKB cross sections $Q^{\text{JWKB}}(v)$. The agreement is exact within the accuracy of the $Q^{\text{JWKB}}(v)$.

Several remarks regarding the use of Eqs. (12) are in order. Firstly, it is necessary that Eqs. (4), together with (9) for $\delta \cong 0$, will represent the actual cross sections over the energy range of interest, i.e., only the r^{-6} long-range term of the potential is significant. Secondly, the use of Eq. (8) requires that the expansions of Eqs. (6) and (7) converge sufficiently rapidly over the energy range of interest.

(Note that the expansions are singular at $E^* = 0$.) The coefficients A_1, \dots, A_4, H_1 were found to be independent of the form of the potential only for a specific class of two-parameter potentials and there is no theoretical reason to believe that they are "unique" or "universal" to all realistic interatomic potentials. In the general case, the best values of $Q(v)$ will be obtained using ϵ^{LJ} and r_m^{LJ} instead of the true values ϵ, r_m , where ϵ^{LJ} and r_m^{LJ} are the potential constants for the L.-J. (12,6) potential which best fits the actual potential over the region of r which most strongly affects the $Q(v)$.

Table II Expansion Coefficients^aCoefficient of terms in the n -th power of E^* for $n = 0, \dots, 6$.

FUNCTION	POTENTIAL	n=0	1	2	3	4	5	6	C.V.(%) ^c
η_m^*	k	-	0.4215587 ^d	-.1655 +.0016	.1057 +.0093	-.0544 +.0160	.0139 +.0084	---	.029
	b	-	0.4146215	-.1653 +.0014	.1073 +.0076	-.0567 +.0131	.0150 +.0069	---	.024
β_g	A	0.947132 ^d	.3657 +.0116	-.277 +.069	.212 +.122	-.078 +.066	---	---	.076
	B	0.945927 ^d	.3613 +.0112	-.275 +.067	.209 +.118	-.077 +.064	---	---	.074
	A	---	25.8464 ^d	-131.6 +15.6	381 +116	-615 +302	503 +328	-162 +126	5.5
	B	---	25.1081 ^d	-129.7 +14.3	387 +107	-642 +279	536 +303	-175 +117	5.2
	A	1 ^d	3.267 +.080	---	---	---	---	---	2.4
	B	1 ^d	3.194 +.068	---	---	---	---	---	2.2

^a Obtained from fit to 20 values ($1 \leq E^* \leq 100$) given by Ref. 37 using forward regression (under of assumption of constant relative error), including all terms significant at the 90% level.

The \pm values indicate 95% confidence interval half widths determined from fit.

^b Potential A is the L.-J. (12,6) while B is the Exp(α ,6) with $\alpha = 13.776$, both corresponding to the same $\kappa = 72$.

^c Coefficient of variation of the fit expressed in %.

^d Fitting was performed with this coefficient constrained to this theoretical value, from Ref. 37.

$$-\frac{d^2 \eta_m^*}{d\beta^2} \beta_g$$

$$\beta_g / g_0 \left[-\frac{d^2 \eta_m^*}{d\beta^2} \beta_g \right]^{1/2}$$

Table III. Comparison of approximate $Q(v)$ from Eq. (12) with $Q^{\text{JWKB}}(v)$ calculation^a

v (Km/sec)	E^*	$Q^{\text{JWKB}}(v) (\text{\AA}^2)$	$Q(v) (\text{\AA}^2)$ ^b
1.585	0.9159	1124	1121
1.63	0.9688	1145	1145
1.73	1.079	1114	1114
1.83	1.221	1017	1016
1.94	1.372	1021	1020
2.05	1.532	1050	1049
2.113	1.629	1031	1030
3.548	4.590	805	805
5.012	9.159	681	681
10.59	40.91	551	552

^a L.-J. (12,6) potential for which, in general, $a_1 = 0.421559$, $g_0 = 0.186299$. Here the specific parameters of the model are $\epsilon = 13.3$ cpe, $r_m = 4.92$ \AA , $C_6 = 2 \epsilon r_m^6 = 3.77 \times 10^5$ cpe - \AA^6 and $\mu = 9,69925 \times 10^{-24}$ g [note: 1 cpe = 1 centipicoerg = 10^{-14} erg.]

^b Calculated from Eq. (12).

IV. FITTING OF EXPERIMENTAL DATA

From Eqs. (4), (8) and (9) it is possible to construct a hierarchy of models for experimental total cross section data, which give successively more information about certain potential parameters, but at the expense of an increasing number of approximations concerning the form of the potential.

From Eq. (8), $Q(v)$ goes through maxima and minima when $\sin \phi = \pm 1$. These extrema are usually indexed^{27b,c} in the order they occur, i.e., $N = 1$ for the first maximum, $N = 1.5$ the first minimum, etc., It has been shown^{27b,c} that this requires (cf. Eq. (8b))

$$\left(N - \frac{3}{8}\right) v_N = \frac{2\epsilon r_m}{\pi \hbar} \left(a_1 + \frac{A_1 \epsilon}{E} + \frac{A_2 \epsilon^2}{E^2} + \dots\right). \quad (14)$$

The first two models to be presented are based upon Eq. (14) and the "experimental" variable $Y \equiv \left(N - \frac{3}{8}\right) v_N$. The third model is based upon Eq. (12).

A. Model I.

It is assumed the extrema indices N and extrema velocities v_N have been determined experimentally. The model for the experiment is

$$Y = I + S_1 X + S_2 X^2 + \dots, \quad (15)$$

where $X = E^{-1}$. A curvilinear forward regression of the experimental data is to be performed, keeping all terms that are significant (at, e.g., the 90% level). In general, the number of terms required to fit Eq. (15) will depend upon the experimental energy range.

Assuming that the expansion $\eta_m^*(E^{*-1})$ of Eq. (6a) holds over the experimental range so that I, S_1, S_2, \dots , are "experimental constants" the following ansatz can be made:^{30b}

$$I = 2a_1 \epsilon r_m / \pi \hbar \quad (16a)$$

$$S_1 = (2\epsilon^2 r_m / \pi \hbar) A_1 \quad (16b)$$

$$\vdots$$

$$S_j = (2\epsilon^{j+1} r_m / \pi \hbar) A_j \quad (16c)$$

With no other assumptions, $a_1 \epsilon r_m$ can be determined from:

$$a_1 \epsilon r_m = \frac{\pi \hbar}{2} I. \quad (2)$$

Under the additional assumption that A_1 and A_2 for the unknown potential are the same as for the "standard" potential (say, the L.-J. (12,6) form), then

$$\epsilon^2 r_m = \frac{\pi \hbar}{2} \frac{S_1}{A_1}, \quad (17a)$$

$$\epsilon = A_1 S_2 / A_2 S_1, \quad (17b)$$

which are the BOB equations (Ref. 30b).

B. Model II

Suppose N and v_N are experimentally determined as above. If, in addition to the assumptions of Model I, it is further assumed that A_1, \dots, A_4 are the same as those of the particular L.-J. (12,6) potential

with the same ϵ and r_m , the model is

$$Y = I + S'_1 Z_1 + \epsilon S'_1 Z_2 + \epsilon^2 S'_1 Z_3 + \epsilon^3 S'_1 Z_4 \quad (18)$$

where $Z_j = A_j / E^j$. Then the following ansatz can be made:

$$a_1 \epsilon r_m = \frac{\pi \hbar}{2} I, \quad (2)$$

$$\epsilon^2 r_m = \frac{\pi \hbar}{2} S'_1. \quad (19)$$

If it is assumed that A_1, \dots, A_4 are known ("universal constants") it is more efficient to use Model II than Model I, since the lower number of free parameters and correct functionality of Eq. (18) leads to smaller confidence intervals of the coefficients I , S'_1 , and ϵ . It should be noted that Models I and II are the same for energies sufficiently high that the last two terms in Eq. (18) can be neglected.

C. Model III

Suppose that Eqs. (8) hold sufficiently well so that H_1 , and A_1, \dots, A_4 are constants over the experimental energy range, namely those for a L.-J. (12,6) potential, and the only contribution to the non-oscillatory cross section is Q_{SLL} . Then the following model for $Q(v)$ results:

$$Q(v) = \gamma_1 v^{-2/5} + \gamma_2 v^{1/2} (1 + \epsilon W_0) \sin \phi, \quad (20a)$$

$$\text{where } \phi = -\frac{3\pi}{4} + \frac{\gamma_3}{v} + \gamma_4 (W_1 + \epsilon W_2 + \epsilon^2 W_3 + \epsilon^3 W_4), \quad (20b)$$

where $W_0 = H_1/E$, and $W_j = A_j/E^j$ for $j = 1, 2, 3, 4$. If the assumptions are valid, then

$$\gamma_1 = p_{SLL}^{(6)} (C_6/\hbar)^{2/5} \quad (21a)$$

$$\gamma_2 = (2\pi r_m)^{3/2} g_0 (\hbar/\epsilon)^{1/2} \quad (21b)$$

$$\gamma_3 = 4 a_1 \epsilon r_m / \hbar \quad (21c)$$

$$\gamma_4 = 4 \epsilon^2 r_m / \hbar \quad (21d)$$

By determining $\gamma_1, \gamma_2, \gamma_3, \gamma_4$ and ϵ from a nonlinear regression of Eq. (21), estimates of C_6, a_1, r_m , and g_0 may be obtained:

$$C_6 = \hbar (\gamma_1 / p_{SLL}^{(6)})^{5/2} \quad (22a)$$

$$a_1 = \gamma_3 \epsilon / \gamma_4 \quad (22b)$$

$$r_m = \hbar \gamma_4 / 4 \epsilon^2 \quad (22c)$$

$$g_0 = \epsilon^{7/2} \gamma_2 / \hbar^2 (\pi \gamma_4 / 2)^{3/2} \quad (22d)$$

Note that if there is a multiplicative bias in the apparent $Q(v)$, i.e., $Q_{\text{true}}(v) = (1 + f) Q_{\text{app}}(v)$ for some constant f , then the values of γ_1 and γ_2 will be biased by exactly the same factor $(1 + f)$.

If a small component due to the C_8 term contributes to $Q(v)$, this may be included in the model by modifying Eq. (20a) to

$$Q(v) = \gamma_1 v^{-2/5} + \gamma_2 v^{1/2} (1 + \epsilon W_0) \sin \phi + \gamma_5, \quad (23)$$

where γ_5 is the $\delta^{(8)}(Q)$ of Eq. (10).

D. Remarks

It may be expected that the value of Model I will decrease as the data extends into the low-velocity range, since the confidence intervals

of the coefficients will become large. This reflects the deterioration of the expansion of Eq. (6a).

While Model II extends the viable range of Eq. (6a) further into the low-velocity region, this is done at the expense of assuming that the potential "resembles" the L.-J.(12,6) functional form. Furthermore, the nonlinearity in ϵ of Eq. (18) will introduce a bias in the confidence intervals calculated by this model.

Model III is the most powerful of the models in that C_6 and g_0 may also be determined (and perhaps C_8); it uses the full set of observed $Q(v)$, and requires no prior graphical analysis. On the other hand, the estimates are more sensitive to contributions from terms of the type $-C_n/r^n$ for $n > 6$, and the model is strongly nonlinear in several parameters ($\gamma_3, \gamma_4, \epsilon$), possibly leading to convergence problems in the fitting procedure, and requiring fairly good initial estimates of the parameters.

In any of the models, the use of the tabulated values of H_1 and A_1, \dots, A_4 for a L.-J.(12,6) potential is tantamount to fitting the parameters dependent upon these quantities to a "standard" functional form of potential. For example, the ϵ obtained from a fit of Model II will not be the best estimate of the actual well-depth of the potential, but the ϵ which leads to the L.-J.(12,6) potential which best approximates the true potential. For this reason there may be differences for potentials which cannot be well-represented by the "standard" form. Furthermore, unless the true potential is close to the standard form, the values of ϵ and r_m will be "experiment-dependent", in the sense that the "best" L.-J.(12,6) potential describing the total cross sections will be different from the best for, say, the differential cross section, as found frequently in the literature. This is, however, a defect of all calculations involving a model potential form.

V. Example Calculations

Three test cases were used to provide examples of the usefulness of Models I and II. Case A is the set of 13 extrema data for the Na-Hg system of Buck et al.^{19b} Cases B and C are hypothetical, representing a L.-J. (12,6) potential with $\epsilon = 8$ cpe, $r_m = 4 \text{ \AA}$, where $\pm 1/2\%$ and $\pm 1\%$ normally distributed errors have been added, respectively to the Q's. Test calculations were carried out for this potential with no added error, giving the expected results. A summary of the calculations appears in Table IV. Cases B and C were intended to mimic case A; for each of the cases there were 13 data in the range $1 < E^* < 10$. (All of the data are in the fairly low velocity range, where the results are expected to be less precise.) It should be noted that the several estimates of $a_1 \in r_m$ obtained for case A are of significantly better precision than the value obtained from the "Buck-inverted" potential for this system.

Examples of the application of Method III are given in Table V. Both cases D and E were L.-J. (12,6) potentials with $\epsilon = 13.3$ cpe and $r_m = 4.92 \text{ \AA}$, with 48 data in the range $1 \leq E^* \leq 40$, with $\pm 1/2\%$ (relative) error in $Q(v)$ added. For both cases D and E, $C_6 = 2 \epsilon r_m^6$, and for case E, $\beta = 1 \text{ \AA}^2$ (i.e., $\gamma_5 \approx 2 \text{ \AA}^2$). From the results it is seen that, at least for this example, Method III is indeed sensitive to the presence of C_8 (even when β is small).

Examination of the results (Tables IV and V) leads to the following conclusions: (1) the error intervals in the fitted parameters decrease successively from Method I through III; (2) a small amount of experimental error induces successively larger errors in $\epsilon^2 r_m$ and in ϵ , when the data are mainly in the low E^* range; (3) the true values of the parameters usually fall within the fitted error intervals.

Listings of FORTRAN IV programs which perform the fitting calculations for Models I, II and III are given in Ref. 40.

Table IV. Example calculations of Models I and II^{a,b}

QUANTITY	CASE A ^c		CASE B ^d		CASE C ^d	
	METHOD I	METHOD II	METHOD I	METHOD II	METHOD I	METHOD II
C.V. (%) ^e	0.31	0.31	0.18	0.25	0.55	0.66
Degree Fitted	3	- -	3	- -	3	- -
$a_1 \in r_m$ (cpe-Å)	18.78 +26	18.75 +14	13.57 +13	13.49 +10	13.98 +39	13.65 +32
$\epsilon^2 r_m$ (cpe ² -Å)	557 +140	561 +57	286 +53	254 +34	442 +157	303 +121
ϵ (cpe)	14.8 +6.2	18.8 +2.4	10.1 +3.7	7.8 +2.5	15.9 +5.0	9.9 +8.0
r_m (Å)	- -	1.6 + .3	- -	4.2 + 2.2	- -	3.1 + 3.8

^a Regressions performed under assumption of constant relative error.

^b + indicate 95% confidence interval halfwidths determined from fit.

^c "True" values from the "full inversion" of the differential cross section data given in Ref. 19b are:

$$a_1 \in r_m = 18.30 + 12\%, \epsilon^2 r_m = 365 + 12\%, \epsilon = 8.8 + 8\%. \quad (\text{the } \epsilon \text{ values probably represent } 70\% \text{ confidence level}).$$

A fit of Eq. (15) including terms to E^{-2} in Ref. 19b gave $a_1 \in r_m = 1.859 + 3\%$,

$$\epsilon^2 r_m = 449 + 6\%, \epsilon = 10.06 + 18\%.$$

^d True values are C.V. = 0.25%, 0.5% respectively, for cases B and C, and $a_1 \in r_m = 13.49$, $\epsilon^2 r_m = 256$,

$$\epsilon = 8, r_m = 4.$$

^e Coefficient of variation of the fit, expressed in %.

^f Degree of polynomial in final fit of Method I.

Table V. Example of the Use of Method III^{a,b}

QUANTITY	TRUE VALUE	INITIAL ^c VALUE	CASE D		CASE E	
			$C_8 = 0^d$	$C_8 \neq 0^e$	$C_8 = 0^d$	$C_8 \neq 0^e$
C.V. (%) ^f	0.25	- -	0.26	0.26	0.39	0.26
$C_6 \times 10^{-5} (\text{cpe-}\text{\AA}^6)$	3.773	3.78	3.777 $\pm .007$	3.753 $\pm .036$	3.776 $\pm .011$	3.752 $\pm .036$
g_0	.186299	.190	.212 $\pm .063$.211 $\pm .072$.213 $\pm .079$.212 $\pm .072$
$\epsilon (\text{cpe})$	13.3	14.0	14.0 ± 1.0	14.0 ± 1.0	14.0 ± 1.5	14.0 ± 1.0
a_1	.421559	0.44	.435 $\pm .036$.435 $\pm .049$.435 $\pm .022$.435 $\pm .049$
$r_m (\text{\AA})$	4.92	4.7	4.5 $\pm .7$	4.5 $\pm .8$	4.5 $\pm .7$	4.5 $\pm .8$
$a_1 \epsilon r_m (\text{cpe-}\text{\AA})$	27.585	28.9	27.62 $\pm .08$	27.62 $\pm .08$	27.62 $\pm .13$	27.63 $\pm .085$
$\epsilon^2 r_m (\text{cpe}^2 - \text{\AA})$	870	921	888 ± 35	889 ± 35	889 ± 52	889 ± 35
$C_8 \times 10^{-5} (\text{cpe-}\text{\AA}^8)$	0 ^g	0	- -	3.8 \pm 5.6	- -	7.4 \pm 5.7

^a Fit performed with assumed constant relative error.

^b \pm indicate 95% confidence interval halfwidths from fit.

^c Fit for $C_8 \neq 0$ was performed using $C_8 = 0$ parameters as initial values.

^d Fit assuming no r^{-8} term is present.

^e Fit assuming a r^{-8} term is present.

^f The coefficient of variation of the fit in %.

^g For case E, $\epsilon = 1.02$.

VI. Concluding Remarks

Total cross sections $Q(v)$ for the scattering of (S-state) atoms⁴¹ in the low-velocity region⁴² contain information primarily on the long-range tail of the interatomic (Σ -state) potential. However, it appears that over the region of r probed by the Q measurements the higher-order terms in the inverse-power expansion of $V(r)$ (i.e., those beyond the leading r^{-6} term) contribute significantly to the potential. Thus it is not in general possible to extract from the smooth $\bar{Q}(v)$ measurements (via the SLL approximation of Eq. (1)) accurate C_6 values without taking cognizance of the $C_8 r^{-8}$ and higher terms. The effect of this deviation from asymptotic r^{-6} dependence over the range of r affecting the experiments is to yield a residual velocity dependence in the "apparent" C_6 calculated via Eq. (1) from the smoothed $\bar{Q}(v)$. Assuming that, for values of $r \gtrsim R(v)$, where $R(v) = (\bar{Q}(v)/2\pi)^{1/2}$, $V(r)$ can be well-approximated by $V(r) \cong -C_6 r^{-6} (1 + \beta r^{-2})$, and provided that over this range $\beta/r^2 \ll 1$, the influence of the r^{-8} term is simply to introduce a constant additive correction $\delta^{(8)}Q$ to the SLL-approximated smoothed cross section.

The glory extrema-velocities and amplitudes are governed largely by the characteristics of the potential well. The results show greatest sensitivity to the "area of the well", which in turn is roughly proportional to the product ϵr_m and is strongly affected by the curvature κ of the potential. The extrema-spacings (i.e., $dN/d(1/v_N)$, in a well-defined limit) yield the quantity $I \propto a_1 \epsilon r_m$ with good accuracy. The primitive BOB analysis (intended to yield $\epsilon^2 r_m$ directly from the glory-velocity data) suffers from the disadvantage that it is tied closely to

the "similar potential" hypothesis, i.e., that the wells are all somewhat "similar" in shape, and, moreover, are similar to those of several commonly used "realistic" interatomic potential functions, for which the expansion coefficients (A_1 , A_2 , etc.) are essentially invariant ("universal") constants.

In the present paper improved procedures are developed for the analysis of $Q(v)$ data. The use of the given values of the expansion coefficients A_1, \dots, A_4 , H_1 , a_1 , g_0 is, however, equivalent to fitting the data to the best "model" potential (of one of the standard forms, such as L.-J.(12,6), $\text{Exp}(\alpha, 6)$, etc.). Applying the methodology to the data of Buck et al.^{19b} on $N(v_N)$ for the well-characterized Na-Hg system indicates that the resulting potential can reproduce the v_N data to within experimental accuracy (here 0.3%). Since the thus-derived potential differs significantly from the best $V(r)$ determined by the Buck inversion procedure employing all scattering data (including differential cross sections, rainbows, etc.), the total cross section data simply do not contain the desired information. At the very least, if both $\Delta Q(v)$ and $\bar{Q}(v)$ data can be reproduced within experimental error by the present procedures, then the data have been essentially fully exploited; the derived potential is by definition "indistinguishable" from the true potential until further data (either extended energy range or angular distributions) can be used to remove the ambiguity.

The literature on neutral atom-atom and atom-molecule scattering from the viewpoint of intermolecular force determinations is extensive and has been reviewed by Bernstein and Muckerman in 1967⁴³ and by Schlier in 1969⁴⁴. In the Appendix is presented an annotated bibliography of recent experimental papers which report total cross sections for systems

involving only atoms and/or hydrogen molecules. The subject of differential cross sections is beyond the scope of this paper but is clearly an extremely important aspect of the general problem of the experimental determination of interatomic potentials.⁴⁵

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APPENDIX

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